Method no.:	PV2106

Target concentration:	45 ppm (205 mg/m^3)

Procedure:	Samples are collected by drawing a known volume of air through a charcoal tube. Samples are desorbed with (95:5) methylene chloride:methanol and analyzed by Gas Chromatography with a Flame Ionization Detector (GC-FID).

Air volume and sampling rate studied:	50 minutes at 0.2 Lpm (10 L)

Status of method:	Partially Validated. This method has been only partially evaluated and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Technical Center has received many requests for a sampling and analytical procedure for Vinyl pyrrolidinone. Charcoal tube sampling and desorption with 1 mL carbon disulfide was tried initially, but the desorption efficiency averaged 38.7%. Desorption with 1 mL (99/1) carbon disulfide/Dimethyl Formamide had concentration dependent desorption ranging from 56.2 to 79.3% for concentrations ranging from 0.104 to 2.08 mg. Desorption with 1 mL (95:5) Methylene Chloride:Methanol averaged 91.5% for concentrations from 0.104 to 2.08 mg. Charcoal tubes had good storage and retention efficiencies. Several manufacturers MSDS recommend a TWA TLV of 100 ppm, so a target concentration of 45 ppm was chosen for this study.

1.1.2 Potential workplace exposure (Ref. 5.1)

Vinyl pyrrolidinone is used to make polymers and coatings.

1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.) (Ref. 5.2)

Rats exposed to Vinyl pyrrolidinone had a LC_{50} of 3200 mg/m^3. The LD_{50} on skin of rabbits was 560 mg/kg, and oral LD_{50} on rats was 1470 mg/kg. In humans, Vinyl pyrrolidinone is an irritant to eyes, skin, and mucous membranes. Chronic exposure to high doses may result in kidney and/or liver damage.

1.1.4 Physical properties (Ref. 5.3)

CAS:	88-12-0
IMIS:	V107
Synonyms:	vinyl pyrrolidone; V-Pyrol; vinyl pyrrolidone; 1-ethenyl-2-pyrrolidinone
Molecular weight:	111.1
Density:	1.04
Freezing point:	13.5 °C
Odor:	mild amine-like
Boiling point:	148 °C
Flash point:	98 °C (209 °F) (open cup)
Color:	colorless to light yellow liquid
Molecular formula:	C_6H_9NO
RTECS:	74507 (UY6107000)

Structure:
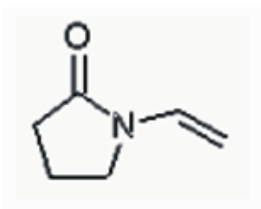
1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 5 ng, with a 1-µL injection volume. This is the smallest amount which could be detected under normal operating conditions.

1.2.2 The overall detection limit is 0.1 ppm based on a 10-liter air volume. (All ppm amounts in this study are based on a 10-L air volume.)

1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical method is reproducible and sensitive.

1.3.3 Reanalysis of samples is possible.

1.3.4 It may be possible to analyze other compounds at the same time.

1.3.5 Interferences may be avoided by proper selection of column and GC parameters.

1.4 Disadvantages

Due to the volatility of the methylene chloride in the desorbing solvent, it may be necessary to have a fan blowing on the autosampler, in order to have consistent injections.

2 Sampling procedure

2.1 Apparatus

2.1.1 A calibrated personal sampling pump, the flow of which can be determined within ±5% at the recommended flow.

2.1.2 Charcoal tubes, lot 120, containing 100 mg adsorbing section with a 50 mg backup section separated by a 2-mm portion of urethane foam, with a silane-treated glass wool plug before the adsorbing section and a 3-mm plug of urethane foam at the back of the backup section. The glass tube containing the adsorbent is 7-cm x 6-mm o.d. and 4-mm i.d., with the ends flame sealed. SKC tubes or equivalent.

2.2 Sampling technique

2.2.1 Open the ends of the charcoal tubes immediately before sampling.

2.2.2 Connect the charcoal tube to the sampling pump with flexible tubing.

2.2.3 Place the tubes in a vertical position to minimize channeling, with the smaller section towards the pump.

2.2.4 Air being sampled should not pass through any hose or tubing before entering the charcoal tube.

2.2.5 Seal the charcoal tube with plastic caps immediately after sampling. Seal each sample lengthwise with a Form OSHA-21 seal.

2.2.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, & transport) except that no air is drawn through it.

2.2.7 Transport the samples (and corresponding paperwork) to the lab for analysis.

2.2.8 Bulks submitted for analysis must be shipped in a separate mailing container from other samples.

2.3   Desorption efficiency

Six tubes were liquid spiked at each loading of 0.104 mg (2.29 ppm), 0.52 mg (11.4 ppm), 1.04 mg (22.9 ppm), and 2.08 mg (45.8 ppm) vinyl pyrrolidinone. They were allowed to equilibrate overnight at room temperature. They were opened; each section placed into a separate 2-mL vial, desorbed with 1 mL of the desorbing solution for 30 minutes with occasional shaking, and then analyzed by GC-FID. The overall average desorption efficiency was 91.5%. (Table 2.3)

Table 2.3
Desorption Efficiency

tube #	% recovery			
	0.104 mg	0.52 mg	1.04 mg	2.08 mg
1	90.2	90.1	93.0	93.6
2	89.6	90.9	92.8	92.3
3	89.3	93.1	92.3	93.0
4	90.3	92.1	90.2	91.9
5	89.2	92.3	91.3	92.2
6	89.1	92.6	92.7	92.6
average	89.6	91.8	92.1	92.6

overall average = 91.5%
standard deviation = ±1.41

2.4   Retention efficiency

Six tubes were liquid spiked with 2.08 mg (45.8 ppm) vinyl pyrrolidinone, allowed to equilibrate overnight, and had 10 liters humid air (91% RH) pulled through them. They were opened, desorbed, and analyzed by GC-FID. Samples were corrected for the desorption efficiency. The retention efficiency averaged 99.2%. There was no vinyl pyrrolidinone found on the backup portion of the tubes. (Table 2.4)

Table 2.4
Retention Efficiency

tube #	% recovered		
	'A'	'B'	total
1	97.8	0.0	97.8
2	99.9	0.0	99.9
3	99.8	0.0	99.8
4	99.4	0.0	99.4
5	99.2	0.0	99.2
6	99.0	0.0	99.0
average			99.2

2.5   Storage

Tubes were spiked with 2.08 mg (45.8 ppm) vinyl pyrrolidinone and stored at room temperature until opened and analyzed. The recoveries averaged 97.9 % for the 14 days stored. (Table 2.5)

Table 2.5
Storage Study

day	% recovered
7	94.4
7	95.6
7	97.7
14	101
14	100
14	98.7
average	97.9

2.6   Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 0.104, 0.52, 1.04, and 2.08 mg/mL vinyl pyrrolidinone. The pooled coefficient of variation was 0.00904. (Table 2.6)

Table 2.6
Precision Study

injection number	0.104 mg/mL	0.52 mg/mL	1.04 mg/mL	2.08 mg/mL
1	6683	31488	61459	120358
2	6723	31405	61674	121914
3	6656	31625	59917	120738
4	6674	31209	60171	119621
5	6704	31461	61713	118677
6	6671	31187	61849	119655
average	6685	31396	61131	120161
standard deviation –	±24.4	±170	±855	±1113
CV –	0.00365	0.00541	0.0140	0.00926
Pooled CV -	0.00904			

Where:

$$CV\ (Coefficient\ of\ Variation) = \frac{standard\ deviation}{average}$$

$$Pooled\ CV = \sqrt{\frac{A1(CV1)^2\ +\ A2(CV2)^2\ +\ A3(CV3)^2\ +\ A4(CV4)^2}{A1\ +\ A2\ +\ A3\ +\ A4}}$$

A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = Coefficients at each level

2.7   Air volume and sampling rate studied

2.7.1   The air volume studied is 10 liters.

2.7.2   The sampling rate studied is 0.2 liters per minute.

2.8   Interferences

Suspected interferences should be listed on sample data sheets.

2.9   Safety precautions

2.9.1   Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.9.2   Safety glasses should be worn at all times.

2.9.3   Follow all safety practices that apply to the workplace being sampled.

3   Analytical method

3.1   Apparatus
3.1.1   Gas chromatograph equipped with a flame ionization detector. A HP 5890 was used in this study.

3.1.2   GC column capable of separating the analyte and an internal standard from any interference. The column used in this study was a 60-m x 0.32-mm i.d. (0.5-µm d_f DB-Wax) capillary.

3.1.3   An electronic integrator or some other suitable method of measuring peak areas.
3.1.4   Two milliliter vials with PTFE-lined caps.

3.1.5   A 1-µL syringe or other convenient size for sample injection.

3.1.6   Pipettes for dispensing the desorbing solution. The Glenco 1-mL dispenser was used in this method.

3.1.7   Volumetric flasks, 5 mL, and other convenient sizes for preparing standards.

3.2   Reagents

3.2.1   Purified GC grade nitrogen, hydrogen, and air.

3.2.2   Vinyl pyrrolidinone, Reagent grade.

3.2.3   Methylene chloride, HPLC grade.

3.2.4   Methanol, HPLC grade.

3.2.5   n-Hexanol, Reagent grade, used as the internal standard.

3.2.6   The desorbing solution is 95/5 methylene chloride/methanol with 0.25 µL/mL n-hexanol internal standard.

3.3   Sample preparation

3.3.1   Sample tubes are opened and the front and back section of each tube are placed in separate 2-mL vials.

3.3.2   Each section is desorbed with 1 mL of the desorbing solution.

3.3.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.4 Standard preparation

3.4.1 Standards are prepared by diluting a known quantity of vinyl pyrrolidinone with the desorbing solution. A standard of 1 µL/mL vinyl pyrrolidinone in the desorbing solution is 1040 µg/mL.

3.4.2 At least two separate standards at the calibration level should be made.

3.4.3 A third analytical standard should be prepared at a higher concentration to check the linearity of the detector. For this study, two standards at 1 µl/mL (1.04 mg/mL) and one standard at 4 µL/mL (4.16 mg/mL) vinyl pyrrolidinone were used.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

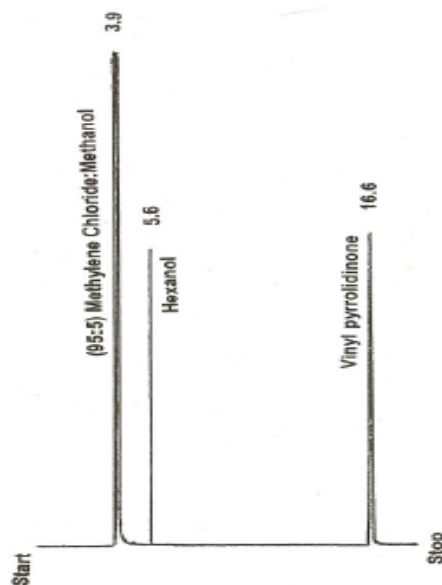| Flow rates	(mL/min)	Temperature	(°C)
Nitrogen (make-up):	30	Injector:	200
Hydrogen (carrier):	2	Detector:	220
Hydrogen (detector):	30	Column:	150
Air:	350		
Injection size:	1 µL		
Chromatogram:			

Figure 1. This is an analytical standard of 1.04 mg/mL Vinyl Pyrrolidinone in (95:5) Methylene Chloride:Methanol with 0.25 uL/mL n-Hexanol internal standard.

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6   Interferences (analytical)

3.6.1   Any compound having the general retention time of the analyte or the internal standard used is interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted if necessary so these interferences will pose no problems.

3.6.2   Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7   Calculations

3.7.1   The instrument is calibrated with a standard of 1.04 mg/mL (1 µL/mL) vinyl pyrrolidinone in the desorbing solution. The linearity of the calibration is checked with a standard of 4.16 mg/mL (4 µL/mL) vinyl pyrrolidinone in the desorbing solution.

3.7.2   If the calibration is non-linear, two more standards must be analyzed so a calibration curve can be plotted and sample values obtained.

3.7.3   To calculate the concentration of analyte in the air sample the following formulas are used:

$$mass\ of\ analyte,\ \mu g\ =\ \frac{(\mu g\,/\,mL)(desorption\ volume,\ mL)}{(desorption\ efficiency,\ decimal)}$$

$$moles\ of\ analyte\ =\ \frac{(mass\ of\ analyte,\ \mu g)(1\,g)}{(molecular\ weight)(10^{6}\ \mu g)}$$

$$volume\ of\ analyte\ =\ (moles\ of\ analyte)(molar\ volume)$$

$$ppm\ =\ \frac{(volume\ of\ analyte,\ L)(10^{6})^{*}}{(air\ volume,\ L)}$$

*All units must cancel.

3.7.4   The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 10-liter air sample:

$$ppm\ =\ \frac{(\mu g\,/\,mL)(DV)(24.46)}{(10\,L)(DE)(MW)}$$

µg/mL = concentration of analyte in sample or standard
24.46 = Molar volume (liters/mole) at 25°C and 760 mmHg
MW   = Molecular weight (g/mole)
DV   = Desorption volume, mL
10 L = 10 liter air sample
DE   = Desorption efficiency, decimal

3.7.5   This calculation is done for each section of the sampling tube and the results added together.

3.8   Safety precautions

3.8.1   All handling of solvents should be done in a hood.

3.8.2   Avoid skin contact with all solvents.

3.8.3   Wear safety glasses at all times.

4   Recommendations for further study

Collection studies need to be performed.

5   References

5.1   Grayson, M., "Kirk Othmer Encyclopedia of Chemical Technology," Third Edition, John Wiley & Son, N.Y., 1981, Vol. 19, p. 616, and Vol. 20, p.220.

5.2   Sweet, D., "Registry of Toxic Effects of Chemical Substances," 1985-86 Edition, U.S. Department of Health and Human Services, Public Health Service, Center for Disease Control, NIOSH, 1987, Vol. 5, p. 4223.

5.3   Sax, N., "Dangerous Properties of Industrial Materials," Fifth Edition, Van Nostrand Reinhold Co., New York, 1979, p. 1089.